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FORMATION OF $CaCO_3$ PARTICLE AND CONDUCTIVITY OF Na_2CO_3 AND $CaCl_2$ SOLUTION UNDER MAGNETIC FIELD ON DYNAMIC FLUID SYSTEM

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Abstract

Hard water causes the $CaCO_3$ scale formation on the pipe walls and heat exchanger equipments in industrial or domestic water processes. A great number of experimental researches on the prevention of the $CaCO_3$ precipitation process by magnetic field have been carried out. In this research, Na_2CO_3 and $CaCl_2$ solutions was magnetized in the circulated flow condition (dynamic fluid system). The velocity of fluid and the circulation time was modified to examine its influences to the magnetization process. $CaCO_3$ content was measured by titration method of EDTA complexometry. Conductivity test was conducted to find out hydrate ion bonding. The results showed that magnetization increased the $CaCO_3$ formation and the optimum process reaches for 10 minutes circulation on 0.554 m/s of flow rate. Magnetic field decreases the conductivities of Na_2CO_3 and $CaCl_2$ solution, hence reduced the ion hydrate bonding. These results showed that magnetization on Na_2CO_3 and $CaCl_2$ ionic solution was effective in controlling the $CaCO_3$ formation by increasing $CaCO_3$ precipitation.

Keywords: $CaCO_3$ conductivity, magnetic carbonate solution, precipitation

1. Introduction

Hard water is a solution which contains high concentration of Calcium and Carbonate ions. The ions cause the scale formation on the pipe walls and heat exchanger equipment, which a serious problem encountered in almost all water processes.

Typical scale deposits consist of minerals that become less soluble with increasing temperature. $CaCO_3$ is the most common deposit. Scale deposits usually form hard-to-remove-linings, which reduce water flow capacities. When they build up on the heat exchanger surfaces, heat transfer efficiency is reduced because of their low thermal conductivity. Anti-scale water treatment using chemical methods changes the solution chemistry and can be very expensive. In some other areas, such as food and beverage industries or residential areas, there are strict requirements for water quality. Thus, environmental protection and economic considerations have become strong motivations for developing various types of physical anti-scale methods, among which are ultrasonic, ultraviolet radiation, electric, and magnetic treatments.

The anti-scale magnetic treatment of hard waters has been employed for more than a half century. According to the review paper of Saksono [1], the efficiency of this treatment is still a controversial question and clear explanation of the phenomenon does not exist yet.

The mechanism on how the magnetic field of relatively low densities precisely modifies the precipitation of low magnetic minerals is still unclear. In many research, $CaCO_3$ precipitation was obtained by reaction of the Na_2CO_3 and $CaCl_2$ solution. Two mechanisms have been developed to address magnetic field effects on calcium carbonate precipitation, viz., (1) a direct effect on dissolved ions and (2) a magnetic effect on particles [2]. They called the first mechanism as "*ionic mechanism*". Higashitani [3] had magnetized Na_2CO_3 solution only in quiescent condition (static fluid system) and then mixed it with $CaCl_2$ solution to obtain the $CaCO_3$ precipitation. He found that the formation of $CaCO_3$ was suppressed but the growth of particle size was accelerated and the portion of aragonite particles arose. Chibowski [4] argued that the hydration energy of an anion CO_3^{2-} is lower than that of a cation Ca^{2+}.

Higashitani [3] hypothesizes that weak bounds of water molecules with the CO_3^{2-} anion (hydrate ion) are quasi-stabilized and structured by the magnetic exposure, so that they inhibit the $CaCO_3$ precipitation rate.

The conductivity of electrolyte solution is able to show the mobility of the existing hydrates ions inside of the solution. The escalating of the conductivity of electrolyte on constant concentration, pressure, and temperature shows that there is a decreasing of hydrate ion diameter which comes with an increasing of hydrate bond strength [5]. With other words, as the escalating of the conductivity increases, the strength of the hydrate ion bond will increase.

Saksono [6] was able to prove that the increasing of the conductivity value of Na_2CO_3 dan $CaCl_2$ solution, a result of the magnetization of the *static fluid systems*, resulted with the decreasing of $CaCO_3$ precipitation. It means that there is an increasing strength of ion hydrate CO_3^{2-} dan Ca^{2+} which makes them harder to form $CaCO_3$.

Dynamic fluid system is the most commercial magnetic devices for control system scale, which treated water flows through a perpendicular magnetic field. Theoretically, in addition to the ionic mechanism effect in static fluid system, Lorentz forces effect occur in the dynamic fluid system. Lorentz force acts on every electrical charged particle (ion), when it moves through the applied magnetic field and and causes essential local shifts movement of ions and possibly to effect the hydrate ion bonding and the precipitation of the ions in the solution [7].

The present study was designed to test and evaluate the effect of magnetic field on Na_2CO_3 and $CaCl_2$ conductivity solution and $CaCO_3$ precipitation in dynamic fluid system. The works explained the effect of magnetic field on hydrat CO_3^{2-} and Ca^{2+} and their precipitation to forming $CaCO_3$ particles.

2. Methods

Water and Electrolytes. Electrolytes $CaCl_2$ and Na_2CO_3 of reagent-grade and deionized water of the resistivity ~18 MΩ, which was obtained from Milli-Q water system were utilized. Unfiltered $CaCl_2$ and Na_2CO_3 0.01 M solutions were prepared by dissolving each electrolyte into the deionized water, and then kept in air-tight bottles in room temperature.

Magnetic treatment on dynamic fluid system. 400 mL of each the sample solution ($CaCl_2$ and Na_2CO_3) was filled into a glass container, to the outflow of which a silicon tube was attached. The tube lead through a laboratory peristaltic pump (Master flex L/STM), was employed to generate fluid flow at variable flow rates (range ca. 0.12–22 mL/sec), then through the treatment area of the system, and back to the container, thus forming a closed, recirculation dynamic fluid system. Neodymium permanent magnets was employed to generate homogeneous magnetic field. A Silicon tubing

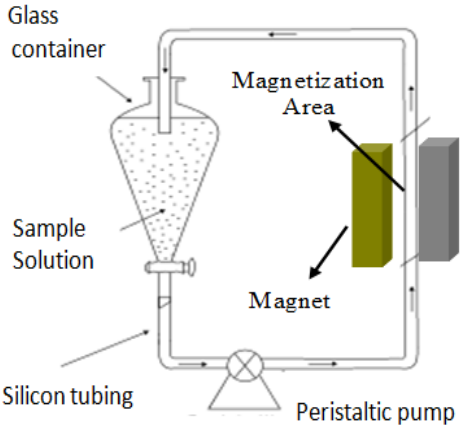

Figure 1. Schematic of the Experimental Treatment System

2 m of total length and 0.7 cm with internal diameter was used. An average magnetic of 5200 Gauss was produced at the gap between the poles in magnetization area. The temperature of the solution in magnetization process equal to the ambient temperature of the surroundings (*i.e.*, room temperature, 28–29 °C). Figure 1 shows a simplified schematic of the experimental treatment system used in the presented work.

In this work, the samples solution which without the circulation and magnetization treatment was conducted to obtain the circulation effect on the conductivity and precipitation of the solutions.

Conductivity and precipitation test. 50 mL of each sample solutions, which were put in glass tube right after the completion of magnetic exposure to obtain the conductivity of solution. Precipitation test was obtained by mixing 10 mL $CaCl_2$ and Na_2CO_3 solutions in precipitation glass reaction tubes. The temperature of the solution was not controlled, and equal to the ambient temperature of the surroundings (i.e., room temperature, 28–29 °C). The Ca^{2+} concentration in the precipitation tube was analyzed by EDTA complexometry (accuracy 0.05 mg as $CaCO_3$), and amount of ions Ca^{2+} consumed in solution as a measure of $CaCO_3$ precipitation.

3. Results and Discussion

The results correlated between the conductivity and precipitation effect on the solutions under magnetic treatment. The effects of circulation time and velocity of fluid is discussed.

The conductivity and precipitation of solution. Figure. 2 shows the characteristics of $CaCl_2$ and Na_2CO_3 conductivity on varied treatment. Ions, like Ca^{2+} and CO_3^{2-}, were covered by H_2O molecules forming hydrated ion. The decreasing of the conductivity of

$CaCl_2$ and Na_2CO_3 solution after the circulation and magnetization process on Figure 2 shows that there was a decreasing of the hydrate ion strength, which was presented by the increasing of the ions precipitation as shown in Figure 3.

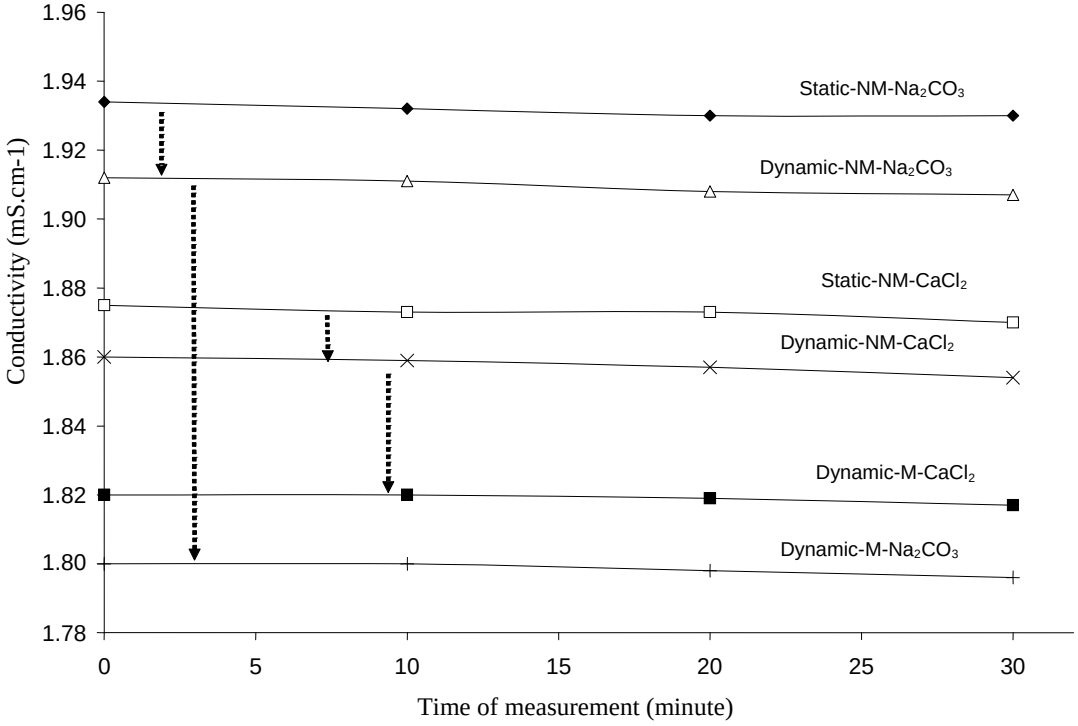

Figure 2. The Conductivity of Na_2CO_3 and $CaCl_2$ Solution for Magnetized (M) and Non-magnetized (NM) Samples Under Static and Dynamic Fluid Systems. The Velocity of Fluid (v) was 0.554 m/s and Circulation Time (t_s) was 10 Min

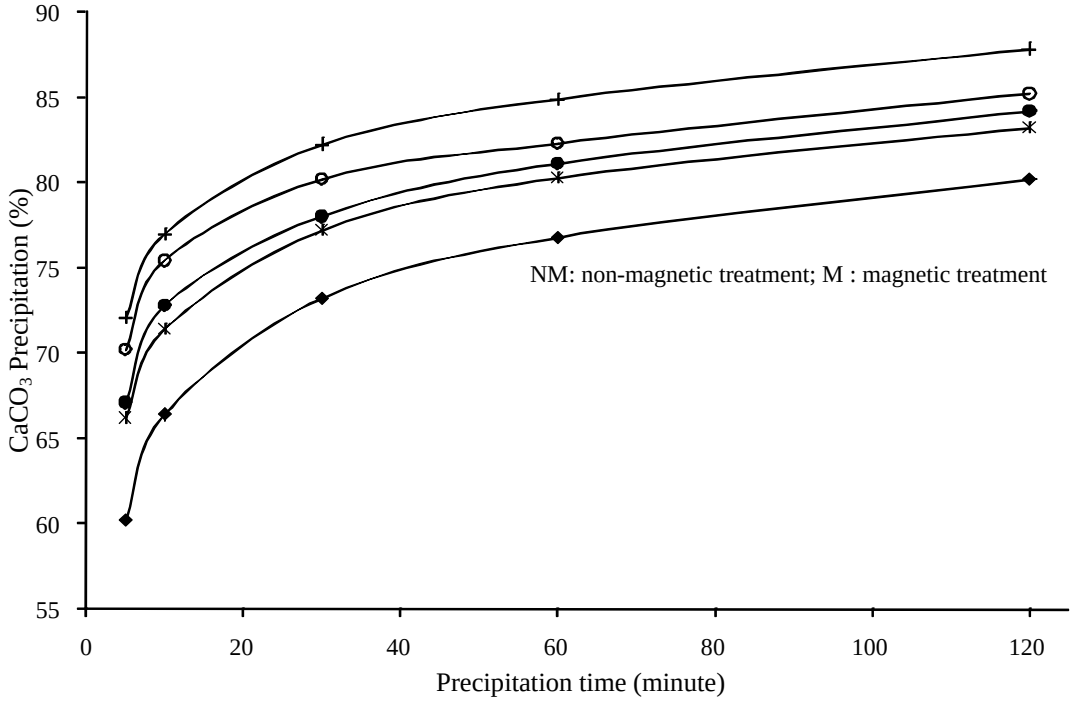

Figure 3. $CaCO_3$ Precipitation of Na_2CO_3 and $CaCl_2$ Mixing Solutions (Treated). Static-NM-Na2CO3 & CaCl12 (♦), Dynamic-NM-Na2CO3 & CaCl12 (✳), Dynamic-M-Na2CO3 (○), Dynamic-M-CaCl2 (●), Dynamic-M-Na2CO3 & CaCl2 (+)

The decreasing of Na_2CO_3 conductivity was much bigger than $CaCl_2$'s decreasing conductivity. Table 1 (2) shows the ion radius (r), hydrate thickness (Δr), and hydration Gibbs energy ($\Delta_{hyd}G$). Holysz [5] found that low value of $(\Delta r/r).\Delta_{hyd}G$ on ion shows a low strenghth of hydrate ion. The value of $(\Delta r/r).\Delta_{hyd}G$ of Na_2CO_3 solution was -1393.7 $kJ.mol^{-1}$ which much lower compared to $CaCl_2$'s about -736.75 $kJ.mol^{-1}$. It shows that the strength of Na_2CO_3 hydrate ion was lower than $CaCl_2$'s so it was easier to be effected by magnetic field. Hence, as the conductivity decreases, the radius of ion hydrate increase.

There was a decreasing of conductivity on Na_2CO_3 solution as a result of the circulation process which shown by Static-NM-Na_2CO_3 and Dynamic-NM-Na_2CO_3 curves on Figure 2. It shows that the mechanical agitation as the circulation flow is able to decrease the hydrate ion strength which able to trigger the ion precipitation that is been shown on static-NM-Na_2CO_3 & $CaCl_2$ curve and dinamic-NM-Na_2CO_3 & $CaCl_2$ curves in Figure 3.

Magnetic field on dynamic fluid system is very effective on lowering sample solution conductivity. As the decreasing of the conductivity become greater, the higher the precipitation Ca^{2+} and CO_3^{2-} ions forming $CaCO_3$.

The most receivable explanation about this phenomenon is that Lorentz forces effect can occur in the dynamic fluid system. Lorentz force acts on every electrical charged particle (ion). When the ion moves through the applied magnetic field, Lorentz force effect causes essential local shifts movement of ions and increasing precipitation Ca^{2+} and CO_3^{2-} ions forming $CaCO_3$.

In kinetic reaction point of view, Saksono [9] has calculated that there is a decreasing of Activation energy (E_a) on $CaCO_3$ formation reaction from the dynamic magnetized sample and the dynamic non-magnetized sample as 10.7 kJ/mol for precipitation temperature of 28 to 70 ^oC, while the decreasing of E_a from the dynamic non-magnetized sample and the static non-magnetized sample as 12.1 kJ/mol. It supports the conclusion that the mechanical agitation and Lorentz force effect are important parts on decreasing Ca^{2+} and CO_3^{2-} ion hydrate strength which makes the formation of $CaCO_3$ increases.

Velocity of fluid. Figure 4 and Table 2 shows the magnetic field effect on the precipitation of $CaCO_3$ increases as flow rate increases. Lorentz force is the main factor that causes weakening effect of ion bond on dynamic fluid system magnetization. On the first 10 minutes of the precipitation, there was an increase in the relative percentage from 10.4% for the flowrate of 0.262 m/s to 11% for the flowrate of 0.792 m/s.

The value of Lorentz (F) is a direct function from ion (e), the velocity of ion translation, magnetic field strength B, which formulated as follows:

$$F = e \times V \times B \quad (1)$$

The increasing flow rate increases the translation velocity of ion crossing the magnetic field. The decreasing effect of hydrate ion interaction caused by Lorents force is shown on the increasing of the precipitation of $CaCO_3$. The turbulent flow which come up with flow rate of 0,792 m/s is able to affect on increasing hydrate ion interaction.

Table 1. Ion Radi (r), Hidrat Ion Thicness (Δr), and Hidration Gibbs Energy ($\Delta G_{Hidration}$) [8]

Type of ion	r (A)	Δr (A)	$-\Delta G_{Hidration}$ (kJ,mol^{-1})
Ca^{2+}	1.00	1.71	1505
CO_3^{2-}	1.78	0.76	1315
HCO_3^-	1.85	0.41	335
Na^+	1.02	1.16	365
Cl^-	1.81	0.43	340

Table 2. $CaCO_3$ Formed at Various Velocity (v) During 10 Minutes Precipitation and Circulation Time Is 10 Minutes

Sample of solution	$CaCO_3$ formed on 10 minutes precipitation (%)		
	(v = 0.262 m/s) Re : 1816	(v = 0.554 m/s) Re : 3840	(v = 0.792 m/s) Re : 5490
Magnetized sample (M)	39.3	70.5	84.7
Non-magnetized sample (NM)	35.2	63.6	76.3
Increases percentage 100 x (M-NM)/NM	10.4	10.8	11.0

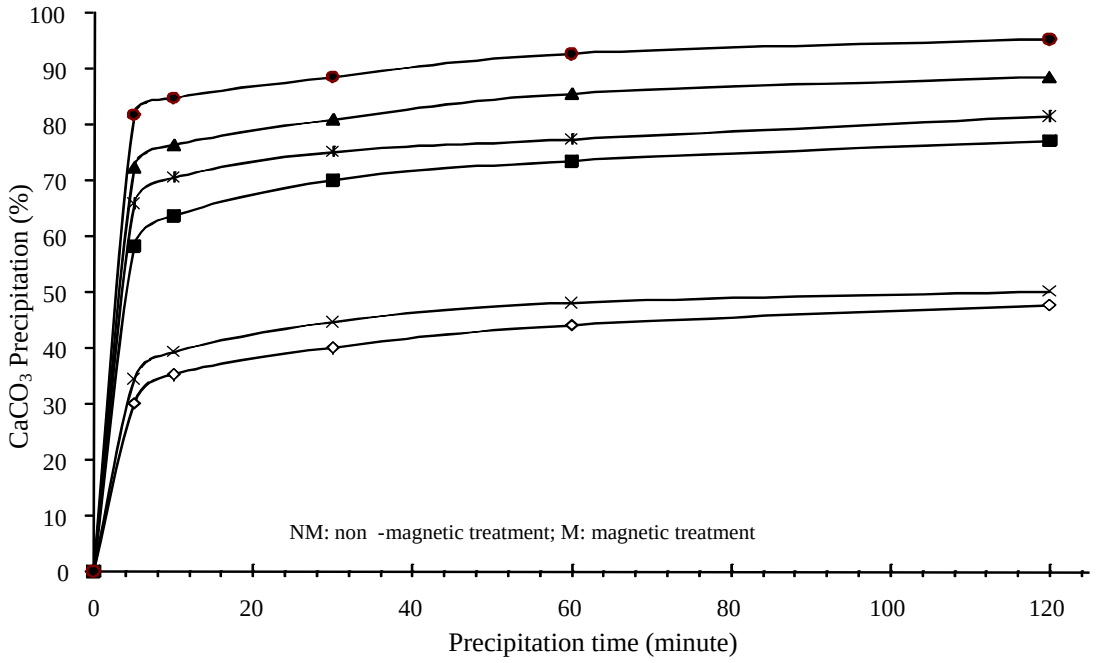

Figure 4. $CaCO_3$ Formed at Various Velocity of Fluid after 10 Minutes of Circulation Time. NM 0.262 m/s (◊), NM 0.554 m/s (■), NM 0.792 m/s (▲), M 0.262 m/s (×), M 0.554 m/s (✳), M 0.792 m/s (●)

The result of Saksono's calculation [9] shows that there is an increase in the formation rate constant of $CaCO_3$ up to 291.7% between the magnetized and the non-magnetized sample of fluid velocity of 0.554 m/s and 5 minutes circulation.

Circulation time. Circulation time is related to the magnetization time which the magnetization time increases as the longer of circulation time. Magnetization time (T_m) is the duration in which the samples is exposed to the magnetic field, which is a of function of Circulation time (T_c), cross sectional area pipe (A), volume sample (V), magnet length (l_m). The correlation has been formulated as follows [10]:

$$T_m = \frac{A.L_m.T_c}{V} \qquad (2)$$

Figure 5 shows that the $CaCO_3$ precipitation increases with the increased circulation time both in magnetic (M) and non-magnetic treatments (NM).

Figure 4 shows the magnetic field effect on the $CaCO_3$ precipitation increases as the addition of the circulation time. The addition of circulation of time (t_s) means the addition of magnetized time and causes the increasing of the weakening effect on hydrate ion. Table 3 shows that the optimum increasing precipitation rate is to be reached on 10 minutes of circulation on which there is a relative increasing percentage up to 8.6%, while on 20 minutes, the relative increasing percentage down to 8.4%. It shows that the optimum condition for magnetized ions on 0.554 m/s flow rate is able to be reached 10 minutes of circulation time.

Fathi [10] used the $CaCO_3$ solution reaching the optimum time of 15 minute with 0.94 L/minutes of flow rate and 1600 Gauss magnetic strength. It shows that the magnetization of de-mineralized water will be saturated on a certain flow rate, length of the magnet, and magnetic strength.

The result of Saksono's calculation [9] shows that there is an increasing constant rate value of $CaCO_3$ formation up to 274.1% between the magnetized sample and the non-magnetized sample at the 10 minutes of circulation time and 0.554 m/s of flow rate. It shows that the magnetization is effective to drive CO_3^{2-} Cl^{2-} ions from Na_2CO_3 and $CaCl_2$ solution to form $CaCO_3$ particle. This process can be used as an application to decrease the hardness of water, which is the main cause of the scale formation.

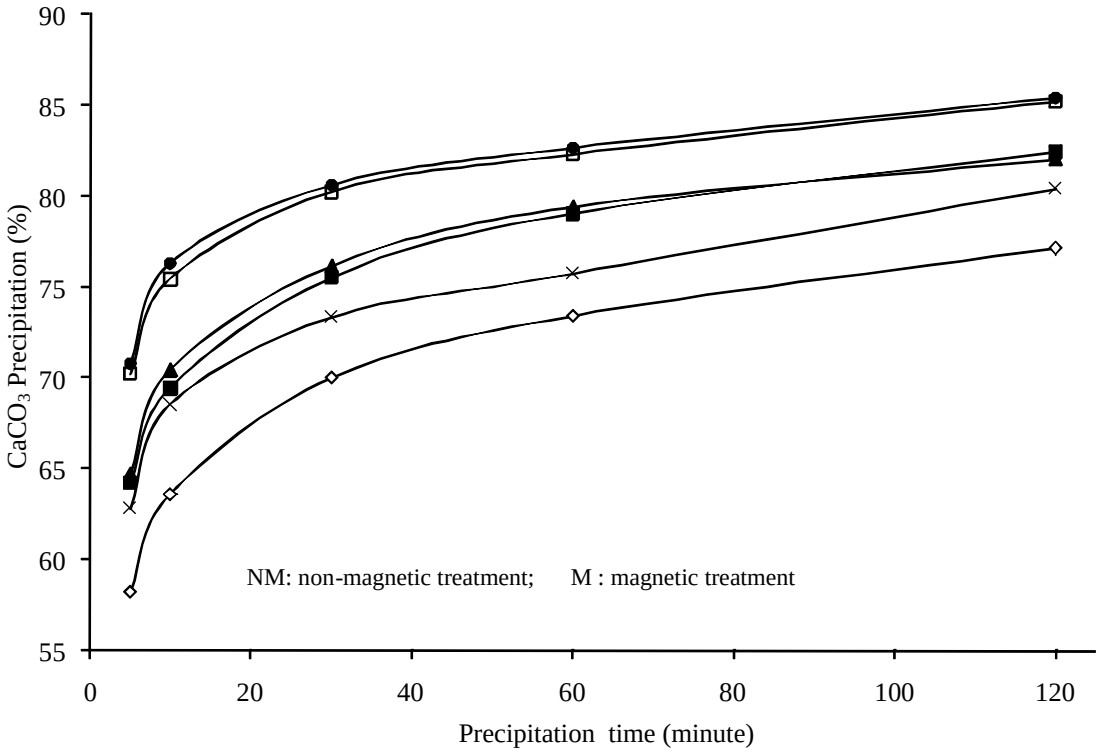

Figure 5. $CaCO_3$ Formed at Various Circulation Time with 0.554 m/s Velocity of Fluid. NM 5 min (◊), NM 10 min (■), NM 20 min (▲), M 5 min (×), M 10 min (□), M 20 min (●)

Table 3. $CaCO_3$ Formed at Various Circulation Time During 10 Minutes Precipitation and Velocity of Fluid is 0.554 m/s

Sample of solution	$CaCO_3$ formed on 10 minutes precipitation (%)		
	5 minutes circulation	10 minutes circulation	20 minutes circulation
Magnetized sample (M)	68.5	75.4	76.3
Non-magnetized sample (NM)	63.6	69.4	70.4
Increases percentage 100 x (M-NM)/NM	7.2	8.6	8.4

4. Conclusion

This research explains the magnetic field effect on the conductivity of Na_2CO_3 and $CaCl_2$ solution and the precipitation to form $CaCO_3$. In our experiments, which had fluid velocity of 0.262 to 0.792 m/s, the magnetization of Na_2CO_3 and $CaCl_2$ solution in dynamic fluid system reduced the conductivity and increase $CaCO_3$ precipitation.

The method is effective in reducing the hardness of water, which is the main cause of the scale formation, by suppressing the amount of CO_3^{2-} and Ca^{2+} ions to form $CaCO_3$ particle.

References

[1] N. Saksono, J. Technol. 20 (2006) 292.
[2] N. Saksono, M. Gozan, S. Bismo, K. Krisanti, W. Widaningrum, S.K. Song, Korean J. Chem. Eng. 25 (2008) 5.
[3] K. Higashitani, S. Kage, S. Katamura, K. Imai, S. Hatade, J. Colloid Interface Sci. 156 (1993) 90.
[4] E. Chibowski, H. Lucyna, A. Szczes, Water Res. 37 (2003) 4685.
[5] L. Holysz, A. Szezes, E. Chibowski, J. Colloid Interface Sci. (2007) 316.
[6] N. Saksono, H. Muhammad, J. Bismo, R. Widaningroem, J. Technol. 21 (2007) 4.

[7] V. Kozic, L.C. Lipus**,** J. Chem. Inf. Comput. Sci. 43 (2003) 1815.
[8] Y. Marcus, Biophys. Chem. (1994) 111.
[9] N. Saksono, Doctoral Dissertation, Univesity of Indonesia, Indonesia, 2008.
[10] A. Fathi, M. Tlili, C. Gabrelli, G. Maurin, M.B. Amor, Water Res. 40 (2006) 1941.